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Ultra-thick, low-stress nanostructured diamond films

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We describe a hot-filament chemical vapor deposition process for growing freestanding nanostructured diamond films, $\sim 80 \mu\text{m}$ thick, with residual tensile stress levels $\lesssim 90 \text{ MPa}$. We characterize the film microstructure, mechanical properties, chemical bond distribution, and elemental composition. Results show that our films are nanostructured with columnar grain diameters of $\lesssim 150 \text{ nm}$ and a highly variable grain length along the growth direction of $\sim 50 - 1500 \text{ nm}$. These films have a rms surface roughness of $\lesssim 200 \text{ nm}$ for a $300 \times 400 \mu\text{m}^2$ scan, which is about one order of magnitude lower than the roughness of typical microcrystalline diamond films of comparable thickness. Soft x-ray absorption near-edge structure (XANES) spectroscopy indicates a large percentage of sp^3 bonding in the films, consistent with a high hardness of 66 GPa . Nanoindentation and XANES results are also consistent with a high phase and elemental purity of the films, directly measured by x-ray and electron diffraction, Rutherford backscattering spectrometry, and elastic recoil detection analysis. Cross-sectional transmission electron microscopy reveals a large density of planar defects within the grains, suggesting a high rate of secondary nucleation during film growth. These films represent a new class of smooth, ultra-thick nanostructured diamond.

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Diamond films are very attractive for many applications such as anti-wear coatings, optical windows, and electrochemical electrodes, where mechanical strength and hardness, optical transparency, and chemical stability are required.¹ A wide range of diamond microstructures has been reported in the literature for the past several decades.¹⁻¹² For example, microcrystalline diamond films, grown by chemical vapor deposition (CVD), can be made hundreds of microns thick and are, therefore, valuable as robust mechanical-wear layers or as free-standing optical windows.²⁻⁴ Nanocrystalline diamond (NCD) and related so-called “ultrananocrystalline” diamond (UNCD), by contrast, have other functional advantages: these are smoother than microcrystalline diamond films and can be made electrically conductive.^{1,5-8} Both NCD and UNCD, however, have previously been demonstrated only in films that are at most a few microns thick.^{1,5-8} Growth of thicker films is often hindered by the development of high stresses during film deposition.¹

In this letter, we report the growth of a new class of ultra-thick nanostructured NCD films. These films have columnar grain diameters of $\lesssim 150 \text{ nm}$, with a highly variable grain length along the growth direction of $\sim 50 - 1500 \text{ nm}$. As a result of this microstructure, our films are much smoother than the (microcrystalline) diamond films of comparable thickness reported previously.^{2,4,9} With the deposition method described in this letter, the grain size does not increase with increasing film thickness, which we attribute to a high rate of secondary nucleation, as evidenced by a high density of planar defects within the grains. Ultra-thick films can be grown because internal stresses in these films are much lower than the stresses which have previously been ob-

served for NCD and UNCD films.^{10,11}

Diamond films were prepared in a CemeCon CC800/Dia hot-filament CVD reactor. Silicon (100) wafers with a thickness of $350 \mu\text{m}$ and a diameter of 50 mm were used as substrates. In order to achieve a high nucleation density, substrates were treated by a bias enhanced nucleation before film growth. A gas mixture of $\sim 3\%$ methane in hydrogen was used as a feedstock gas for growth. Additionally, oxygen was inserted periodically to the gas mixture with an average concentration of $\sim 1\%$ in order to obtain nanocrystalline growth. Parallel tungsten filaments were electrically heated to a temperature of 1950°C and served as a deposition source. Their distance to the substrate was $\sim 10 \text{ mm}$. The substrate was heated only by thermal radiation of the filaments to a temperature of $\sim 750^\circ\text{C}$. The gas pressure was fixed at 5 mbar during deposition. With these deposition conditions, we attained an average growth rate of 165 nm/h . The deposition of the $\sim 80\text{-}\mu\text{m}$ -thick film took altogether ~ 483 deposition hours divided up into 11 single runs.

As-deposited films were mechanically removed from Si substrates and characterized by several complementary techniques. Mechanical testing was done with a Hysitron TriboIndenter nanoindentation system. A Berkovich diamond indenter and a maximum load of 250 mN were used. The load-unload data were analyzed using the method of Oliver and Pharr¹³ to extract the hardness and elastic modulus. The microstructure was studied by bright-field (BF) and dark-field (DF) cross-sectional transmission electron microscopy (XTEM) in a Philips CM300FEG transmission electron microscope (TEM) operating at 300 kV . A focused ion beam instrument was used to prepare TEM cross-sections. Soft x-ray absorp-

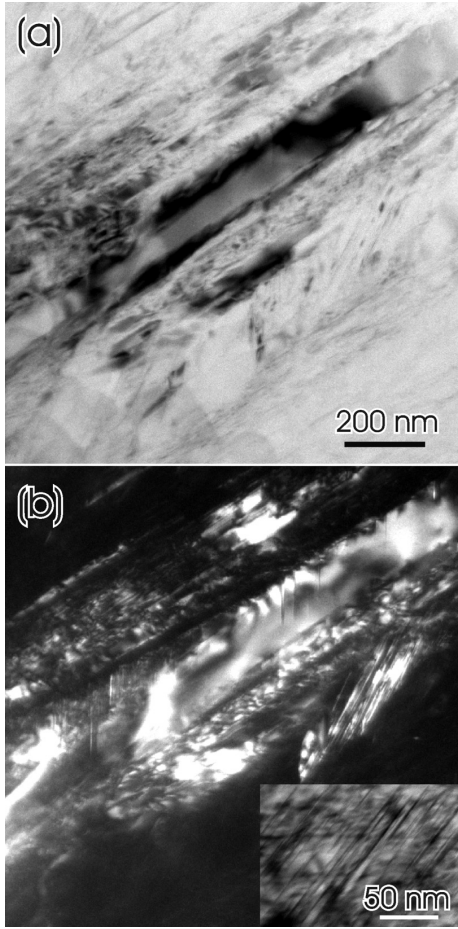


FIG. 1: Bright-field (a) and dark-field (b) XTEM images of the nanostructured diamond film, showing an area of the cross-section with a large, elongated crystallite and a number of smaller crystallites. Both images are of the same magnification. The inset in (b) shows a higher magnification bright-field image of the film.

tion near-edge structure (XANES) spectroscopy experiments were performed at undulator beamline 8.0 at the Advanced Light Source, Lawrence Berkeley National Laboratory.¹⁴ Spectra were obtained by recording the total electron yield. After a linear background subtraction, all XANES spectra were normalized to the post-edge step heights. The monochromator was calibrated by aligning the π^* resonance in the C K -edge of highly oriented pyrolytic graphite (HOPG) to 285.38 eV. The 4 MV ion accelerator (NEC, model 4UH) at LLNL was used for Rutherford backscattering (RBS) spectrometry and elastic recoil detection analysis (ERDA), which were done with 2.0 and 3.0 MeV $^4\text{He}^+$ ions, respectively. Infrared (IR) transmission was measured with a Thermo-Nicolet Nexus 470 FT-IR E.S.P. system operating in transmission mode.

Following deposition, NCD films showed no evidence of delamination from the Si substrates, suggesting low film stress. This has been verified by a direct measure-

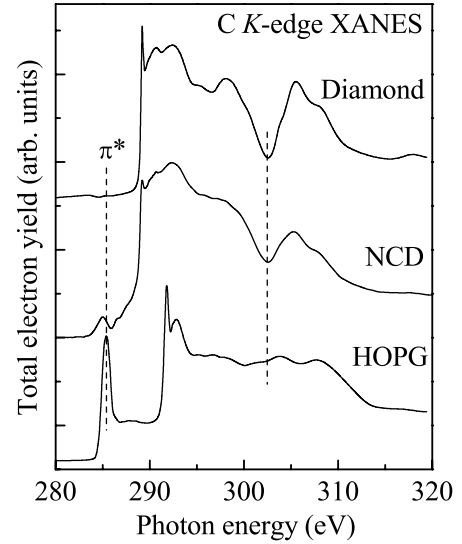


FIG. 2: Carbon K -edge XANES spectra of a clean type IIB conducting diamond (111) single crystal, our nanocrystalline diamond (NCD) film, and graphite (HOPG).

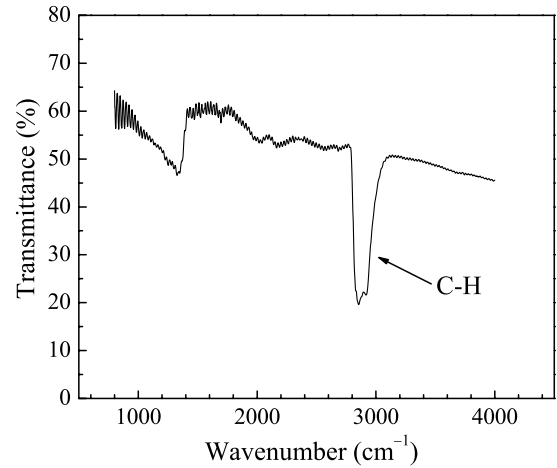


FIG. 3: Transmission IR spectrum of the nanocrystalline diamond film. High frequency oscillations are attributed to the microcavity effect. The broad absorption band at $\sim 2875 \text{ cm}^{-1}$ is attributed to the presence of a relatively small fraction of sp^3 hybridized monohydride (C-H) groups.

ment by the wafer bending method with a Tesa μ white 100 height gauge and the calculation of the stress by Stoney's formula,¹⁵ yielding tensile stresses of $\lesssim 90 \text{ MPa}$ for an $\sim 80\text{-}\mu\text{m}$ -thick film. Scanning white light interferometry measurements reveal relatively smooth surfaces with a rms surface roughness of $\lesssim 200 \text{ nm}$ for a $300 \times 400 \mu\text{m}^2$ scan.¹⁶ The fact that the surface remains relatively smooth even for thick films indicates a high secondary

nucleation rate during film deposition. Indeed, microcrystalline diamond films of a comparable thickness typically have significantly larger roughness^{2,9} and, typically, a grain size of about one third of the film thickness (i.e., $\sim 25\ \mu\text{m}$ grains for an $\sim 80\text{-}\mu\text{m}$ -thick film).

A nanoindentation study of our NCD films has yielded hardness and Young's modulus values of 66.5 ± 0.6 and 609.2 ± 3.0 GPa, respectively.¹⁷ These values are comparable with hardness and Young's modulus of 80.2 ± 1.5 and 709.6 ± 8.9 GPa, respectively,¹⁷ obtained with the same nanoindentation setup for a reference optical-quality thick microcrystalline diamond sample.¹⁸

Electron diffraction in the TEM and x-ray diffraction (with a Cu $K\alpha$ source) have revealed no evidence of other phases of carbon (such as possible graphite crystallites or amorphous carbon) in our NCD films in addition to the expected cubic diamond phase. Moreover, no signals from possible W and O impurities have been observed in RBS spectra from NCD films, indicating that W and O contaminants, if present, are at levels $\lesssim 0.005$ and 0.5 at.%, respectively. Such a high phase and elemental purity is consistent with the excellent mechanical properties of our NCD films discussed above.

The microstructure of the NCD film is illustrated in XTEM images in Fig. 1, showing an area with the largest crystallite that we have observed examining three TEM cross sections extracted from different parts of the NCD film. A comparison of BF [Fig. 1(a)] and DF [Fig. 1(b)] images taken from the same area of the cross section illustrates the nanostructured character of the film. Typical columnar grain dimensions are $20\text{--}150$ nm and $50\text{--}1500$ nm in the film plane and in the growth direction, respectively. In almost all the grains, a large concentration of planar defects has been observed, as can clearly be seen for several individual grains in images in Fig. 1. Such planar defects are better illustrated in a higher magnification BF image in the inset in Fig. 1(b). Somewhat similar planar defects have previously been observed in plan-view TEM studies of thin NCD and UNCD films.^{1,10} Our detailed XTEM investigation of the atomic structure of such planar defects is in progress and will be reported separately.

To estimate the relative sp^2/sp^3 bond fraction, NCD films were studied by XANES spectroscopy. Figure 2 gives a comparison of C K -edge XANES spectra of HOPG, the NCD film, and a diamond single crystal. Such XANES spectra reflect angular-momentum-selected electronic transitions from the C $1s$ core level into the conduction band and, hence, essentially map the p -projected density of empty states in the solid above the Fermi level.¹⁹ In addition, a sharp peak at ~ 289.2 eV in spectra from the NCD film and the diamond single crystal is commonly attributed to the C $1s$ core exciton.²⁰ Both the core exciton peak at ~ 289.2 eV and a dip at ~ 302 eV in the p -projected density of states of diamond are often used to evaluate the quality of diamond.^{20,21} A comparison of spectra for the NCD film and a diamond

single crystal in Fig. 2 provides further evidence of the good quality of our NCD films. The small, broader peak at ~ 285.4 eV in Fig. 2 in the NCD spectrum is assigned to the $1s \rightarrow \pi^*$ transition of π -bonded carbon (i.e., sp^2 carbon).^{19,20} The low intensity of this sp^2 -related π^* peak in the XANES spectrum of NCD (compared to its intensity in the spectrum from graphite also shown in Fig. 2) clearly demonstrates that sp^3 -type bonding is dominant in our NCD films. The relative fraction of sp^2 bonds of $\sim 10\%$ in NCD films can be roughly estimated by taking the ratio of the intensities of the π^* peak at ~ 285 eV and the broad σ^* resonance at ~ 291 eV. This result is not unexpected since C atoms at grain boundaries in NCD and UNCD are typically sp^2 hybridized.¹ However, the above rough estimate gives only the upper bound of the bond fraction since sp^2 -bonded surface C atoms also contribute to the π^* peak in Fig. 2.²⁰

Finally, since film transmittance is important for optical applications, we have measured the transmission IR spectrum of the NCD film (Fig. 3). This spectrum reveals a broad C–H stretch band centered at $\sim 2875\text{ cm}^{-1}$ with a full width at half maximum of $\sim 150\text{ cm}^{-1}$. This is consistent with ~ 1 at.% of H in our films directly measured by ERDA. The fact that the C–H stretch mode lies below 3000 cm^{-1} indicates that hydrogen is bound to sp^3 hybridized carbon atoms. Furthermore, in view of the relatively low hydrogen content in our NCD films, tertiary C–H (monohydride) groups seem to be the most likely cause for the 2875 cm^{-1} band. Indeed, monohydride terminated diamond surfaces exhibit C–H stretch modes at $\sim 2838\text{ cm}^{-1}$ [C(111) surface]²² and 2928 cm^{-1} [C(100) surface],²³ respectively. Thus, we attribute the broad absorption band at $\sim 2875\text{ cm}^{-1}$ to the presence of a relatively small fraction of sp^3 hybridized monohydride groups. Besides the C–H related absorption, the $80\text{-}\mu\text{m}$ -thick-film is remarkably transparent. In fact, the absolute IR transmittance of our film is comparable to that previously obtained for films that are only $\sim 4\ \mu\text{m}$ thick.²⁴

In summary, we have synthesized ultra-thick and relatively smooth nanostructured diamond films through a hot-filament CVD process. In our films, sp^3 -type bonds are dominant, and residual stress, hardness, and Young's modulus are among the best reported for NCD films. These ultra-thick films are appropriate for a variety of optical and mechanical applications.

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 - ¹⁷ Error bounds for hardness and Young's modulus are standard deviations over 5 consecutive nanoindentation tests.
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